

# Synchrotron X-ray Absorption of LaCoO<sub>3</sub> Perovskite

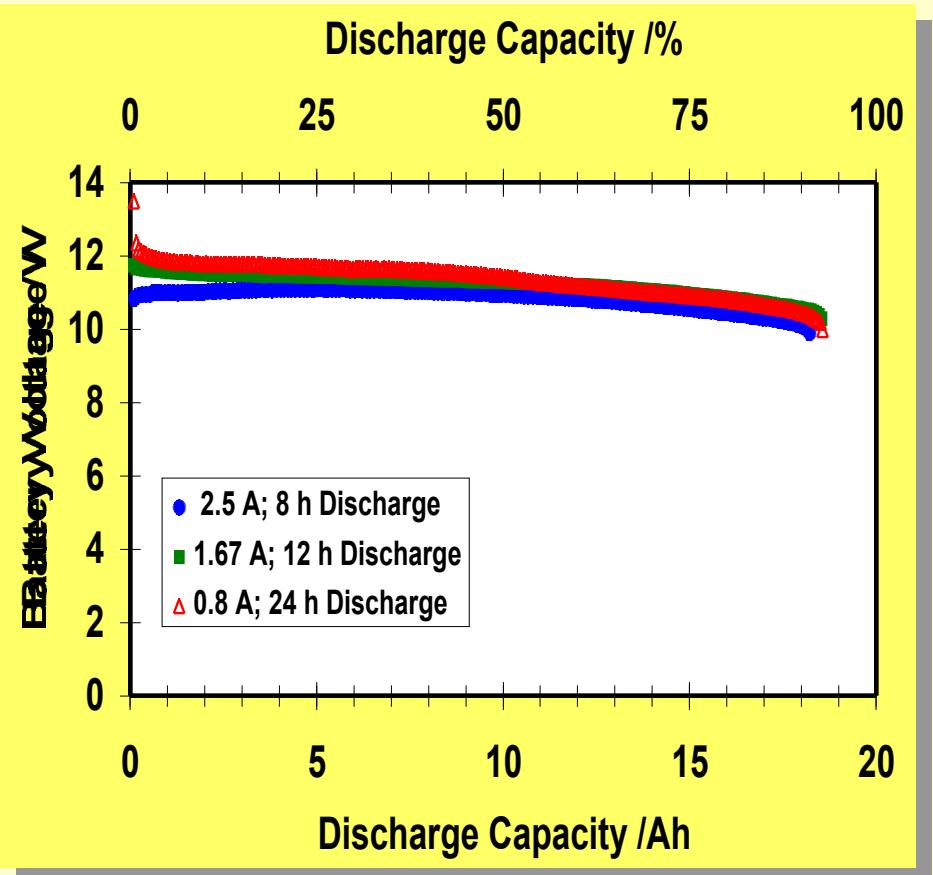
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USA

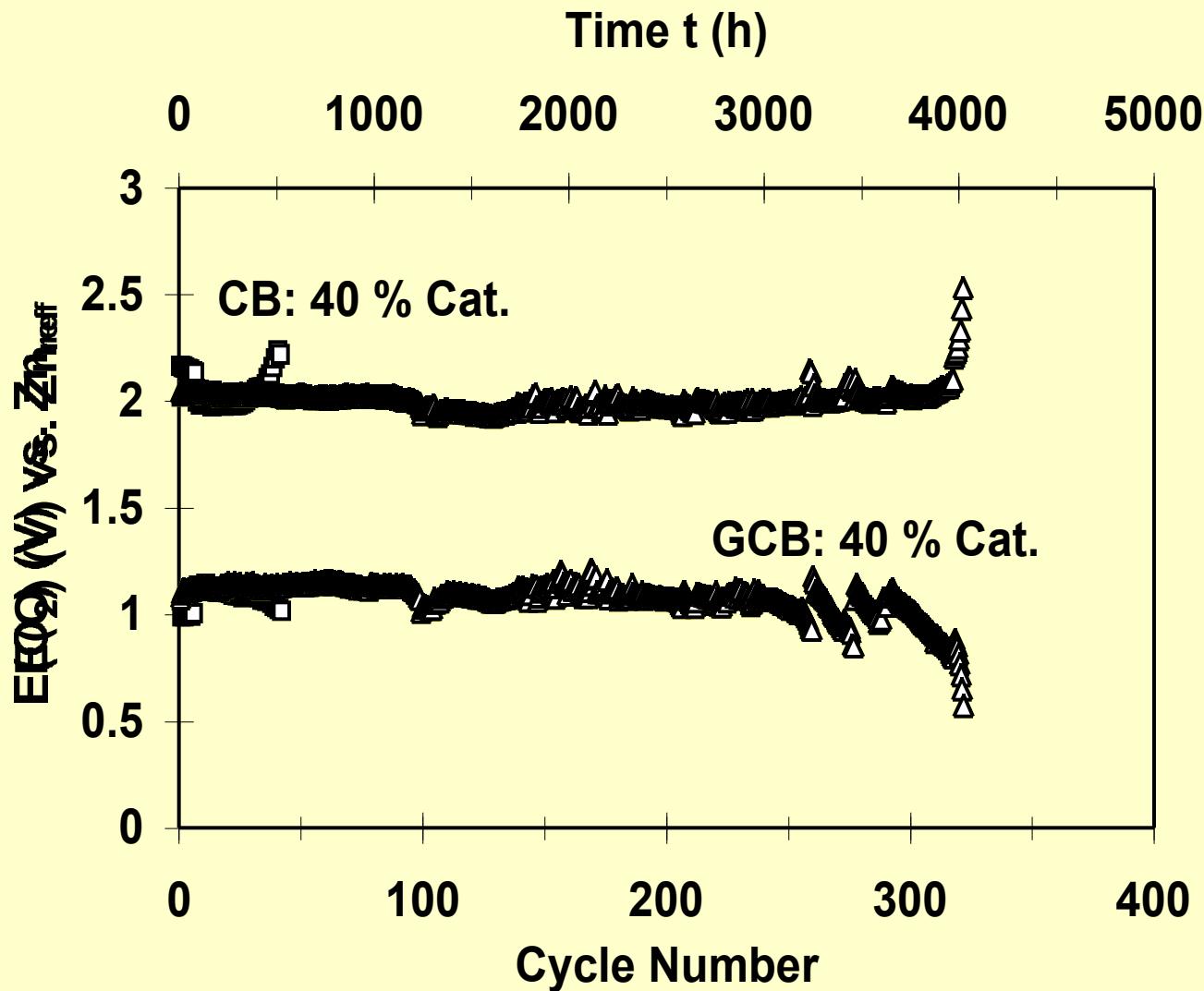
## Content

- Zinc/air battery
- Electrode preparation
- XANES and EXAFS spectra of La<sub>0.6</sub>Ca<sub>0.4</sub>CoO<sub>3</sub>
- XANES spectra of the oxygen electrode
- Pre-edge spectra of LaCoO<sub>3</sub>
- EXAFS spectra LaCoO<sub>3</sub>
- EXAFS simulation using FEFF8 code

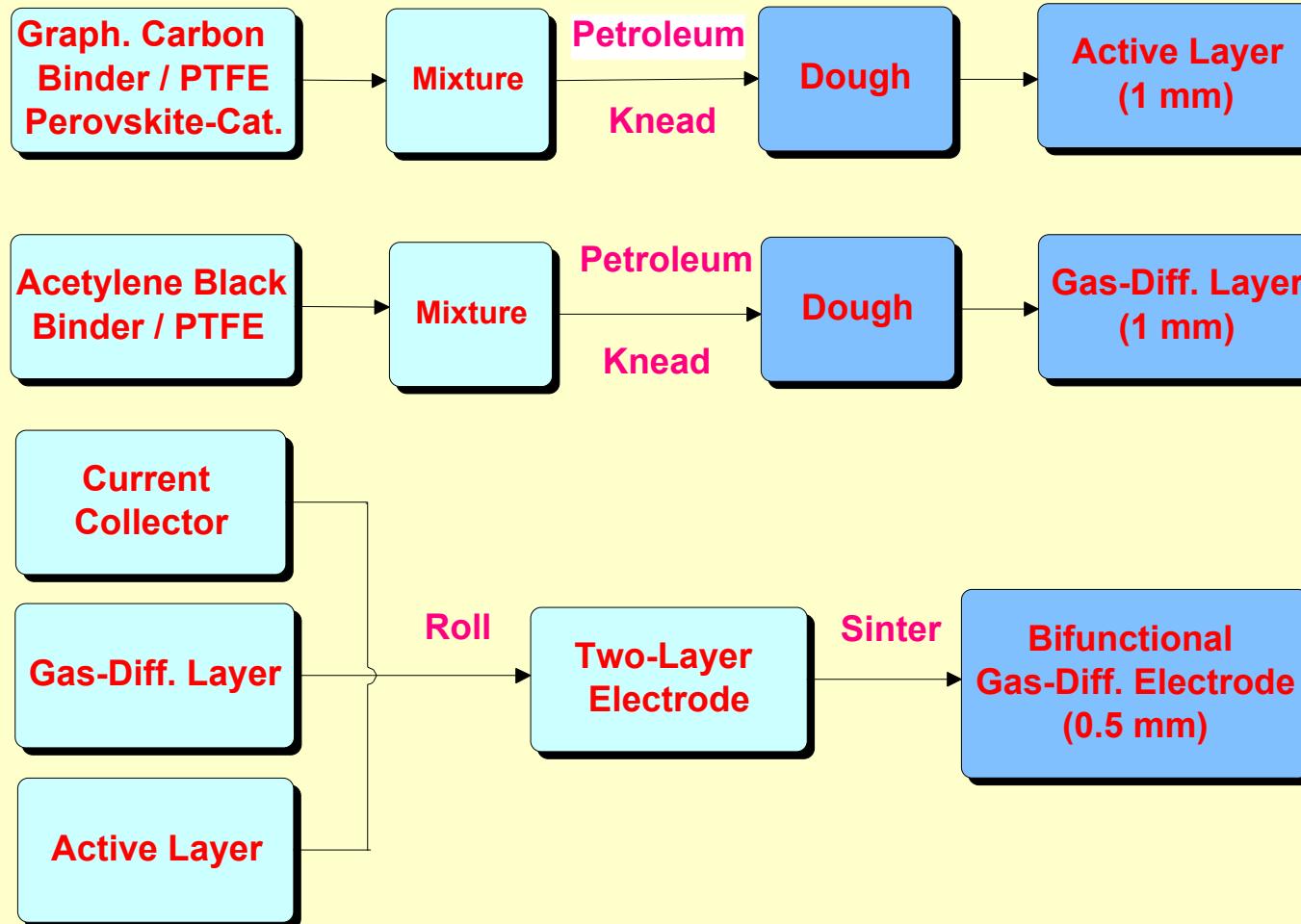
## Rechargeable Zinc/Air-Battery

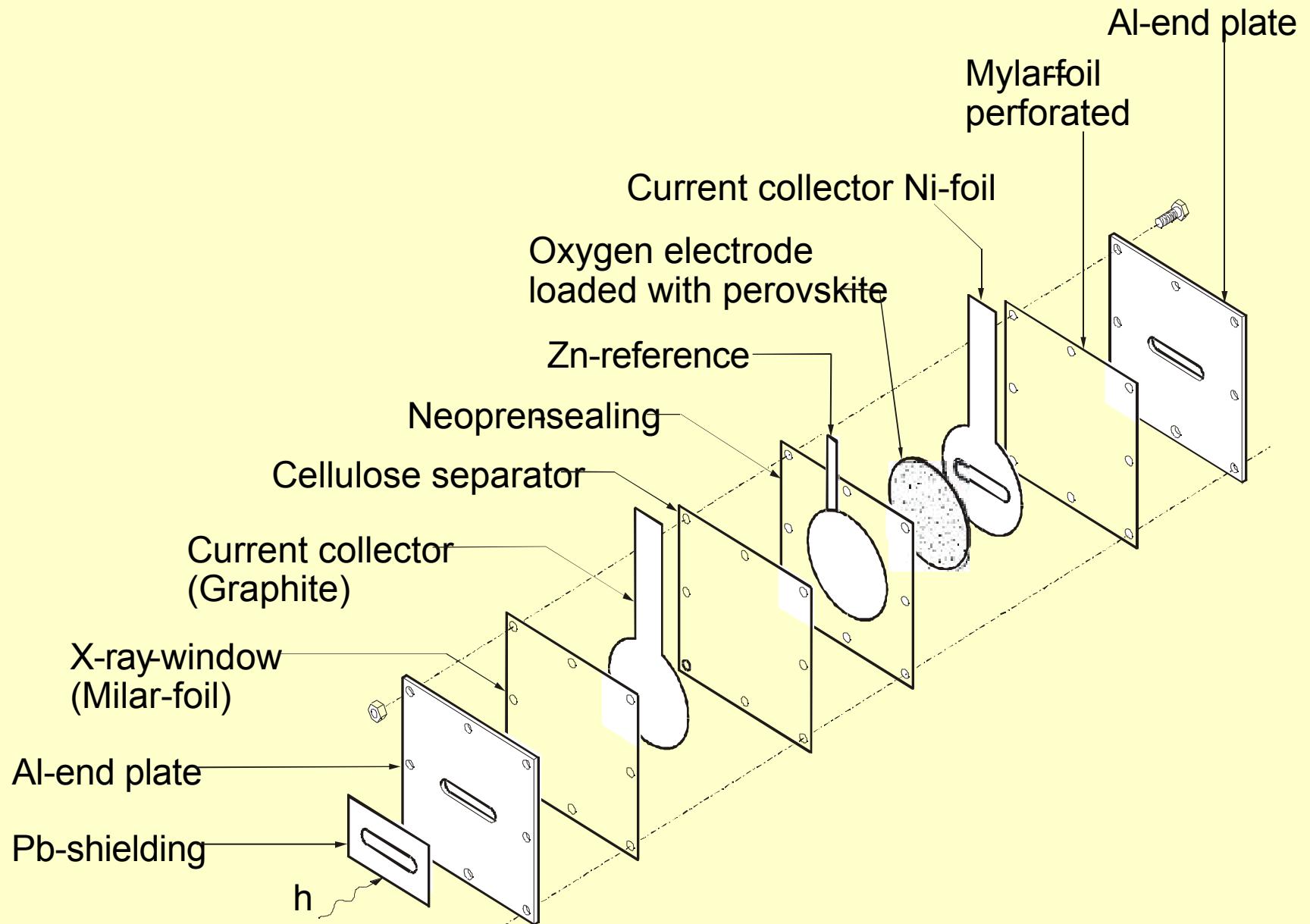


## Cycle life of the oxygen diffusion electrode



## Preparation of the Gas-Diffusion Electrodes





# Preparation of the Catalyst

**Catalyst: powder of  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$**

Thermal decomposition of the amorphous citrate precursor  
At 700°C (1M citric acid + nitrates of La , Ca and Co)

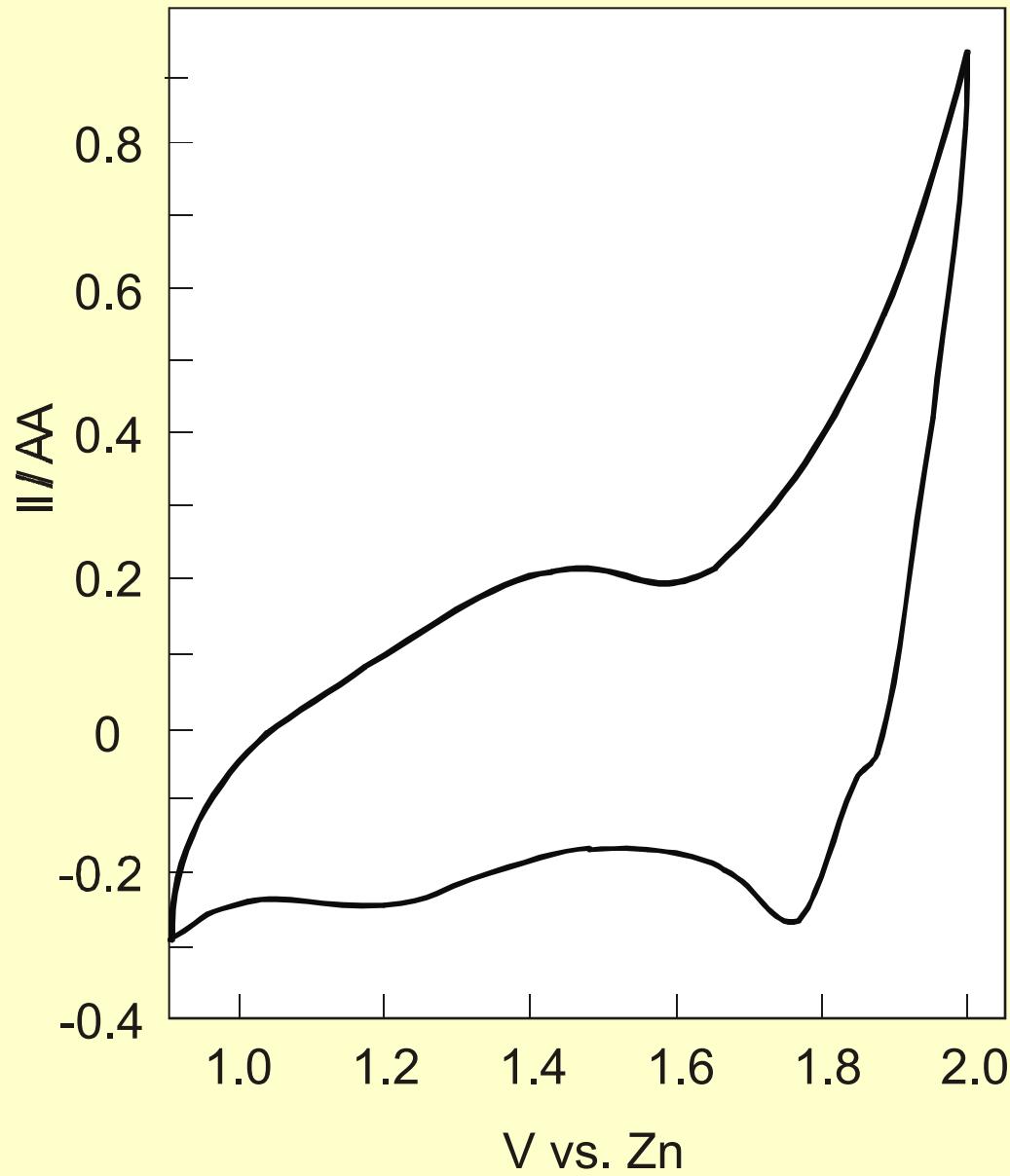
**Incorporation in the Electrodes :**

mixture of graphite Vulcan XC 72 + catalyst + Binder  
(Ratio  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  : Vulcan XC72 = 1:1)

deposited on the substrate e.g. Ni-net

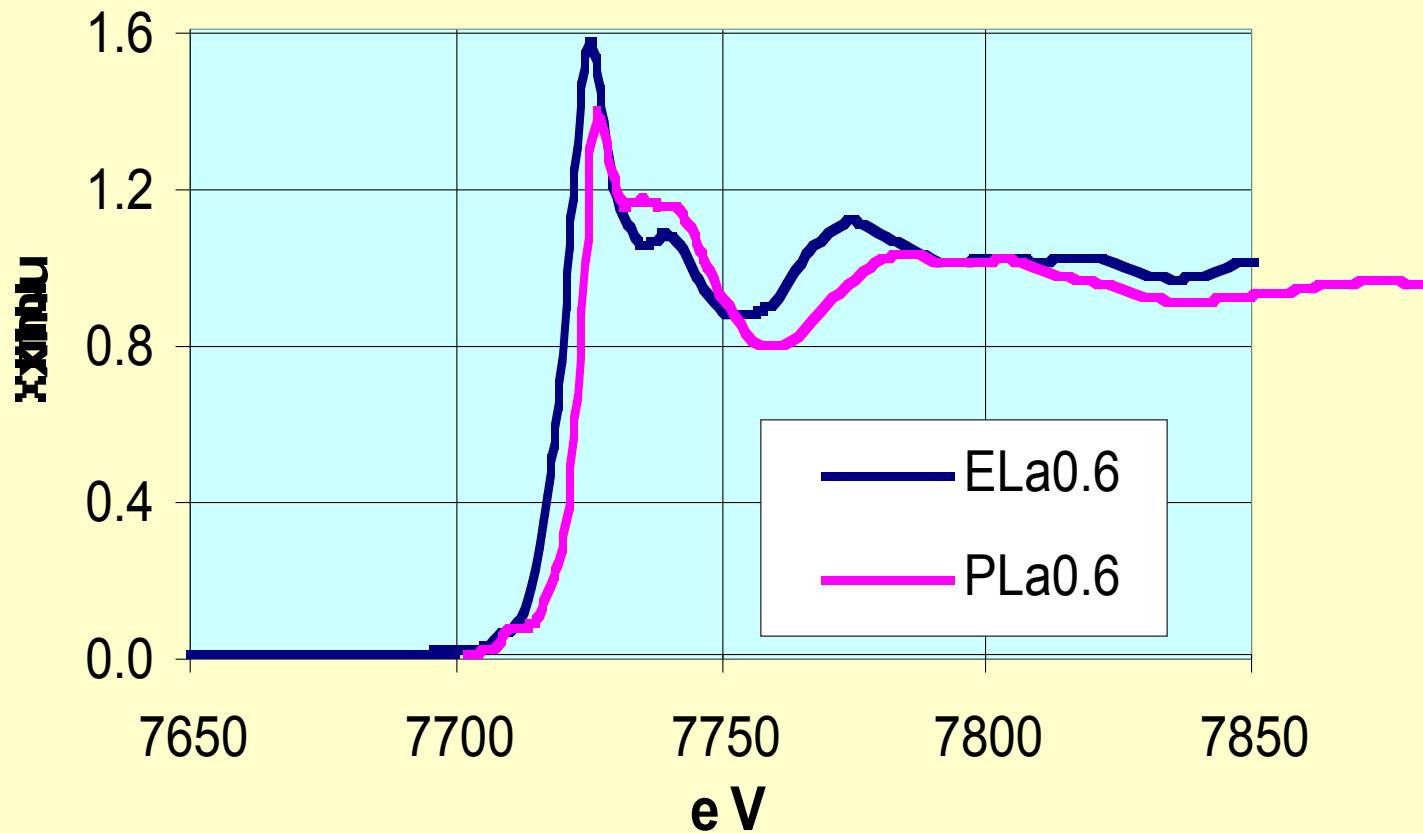
Dried in air

Heated at 300 °C for 2h

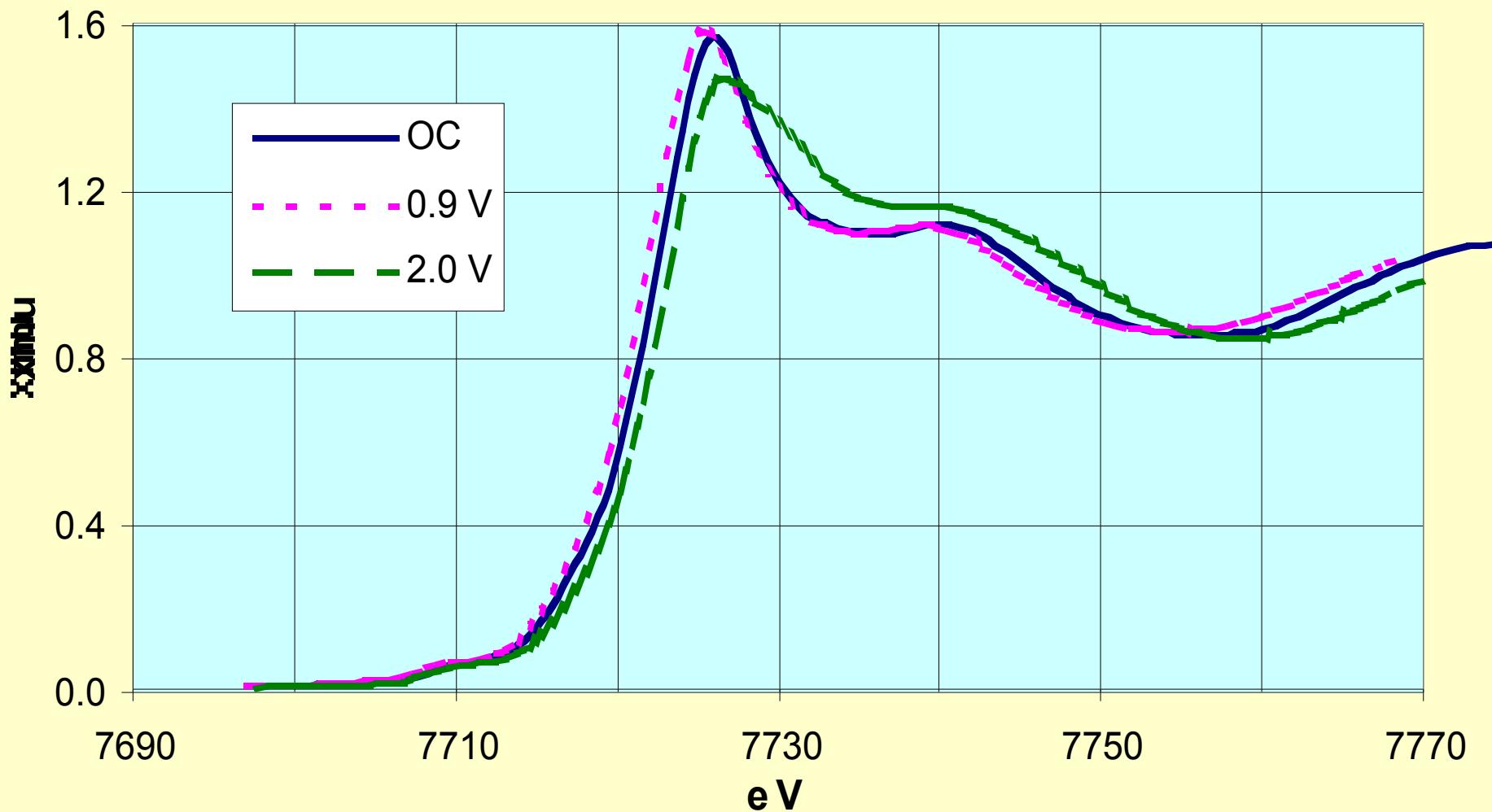


Cyclic Voltammogram of  
a  $\text{La}_{0.6} \text{Ca}_{0.4} \text{CoO}_3$   
loaded oxygen electrode

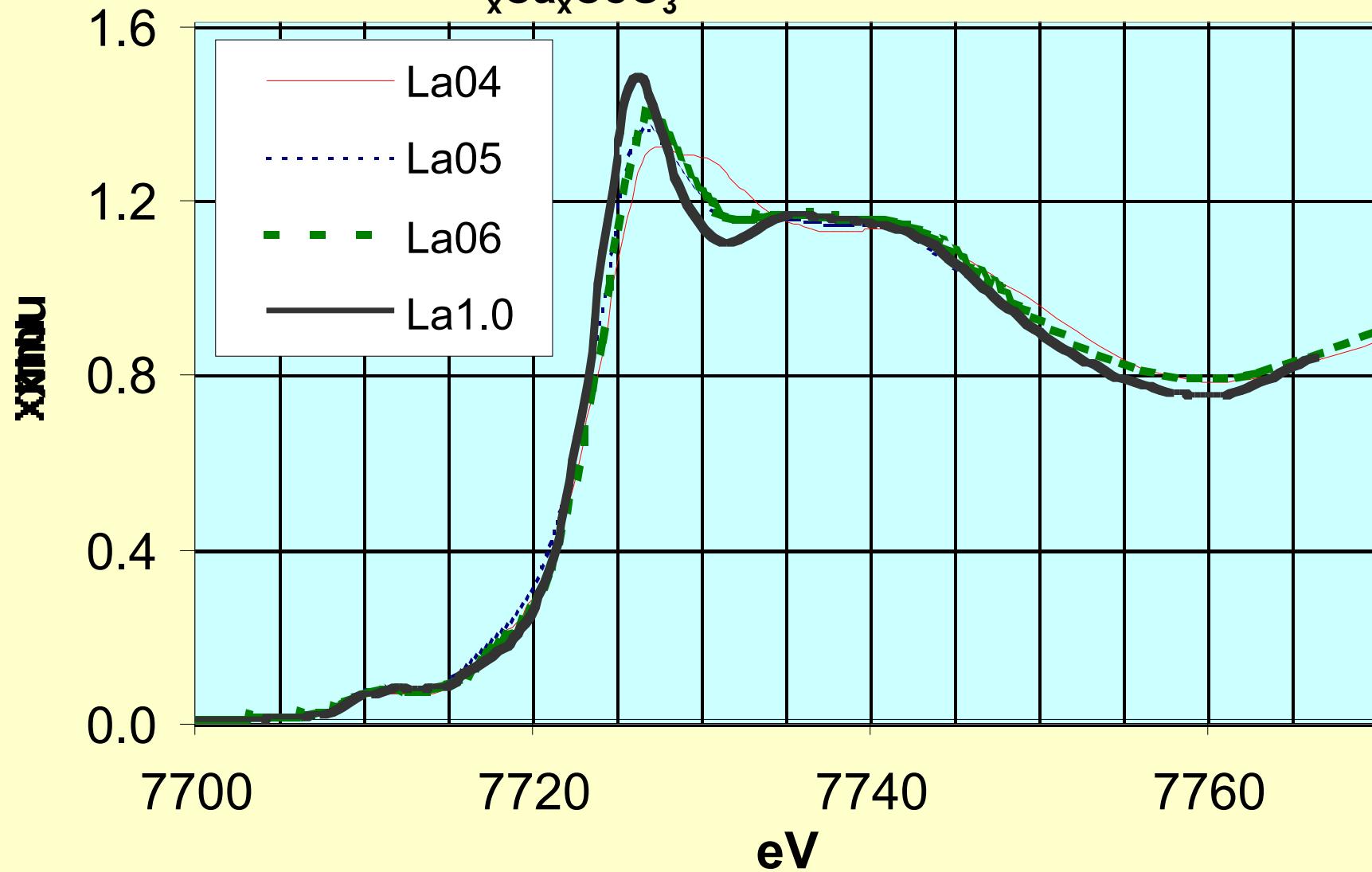
**$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  as a powder and incorporated in  
an Electrode prepared at 340°C**

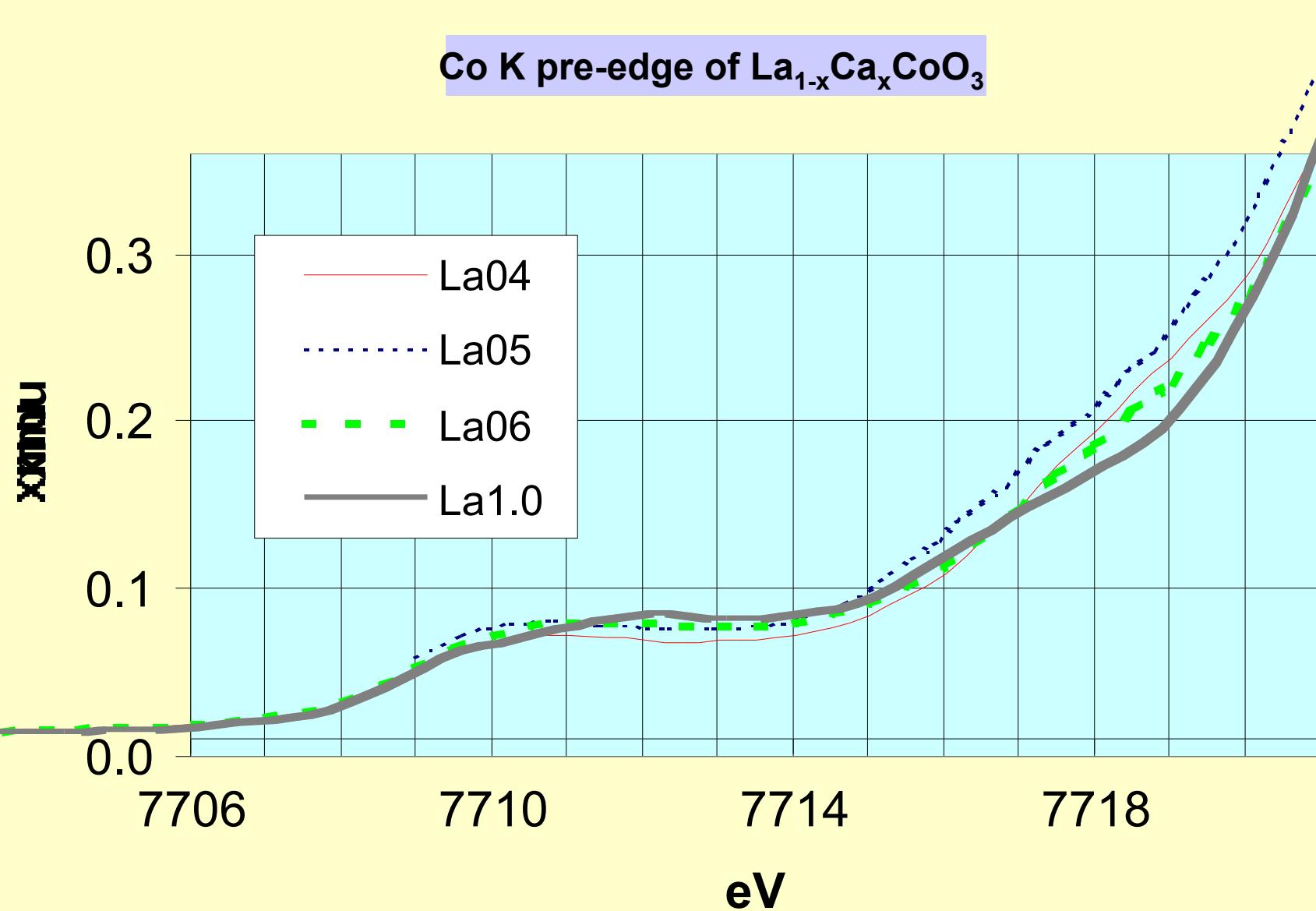


In-situ XANES-spectra of a  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  catalyzed oxygen electrode measured at different electrode potentials



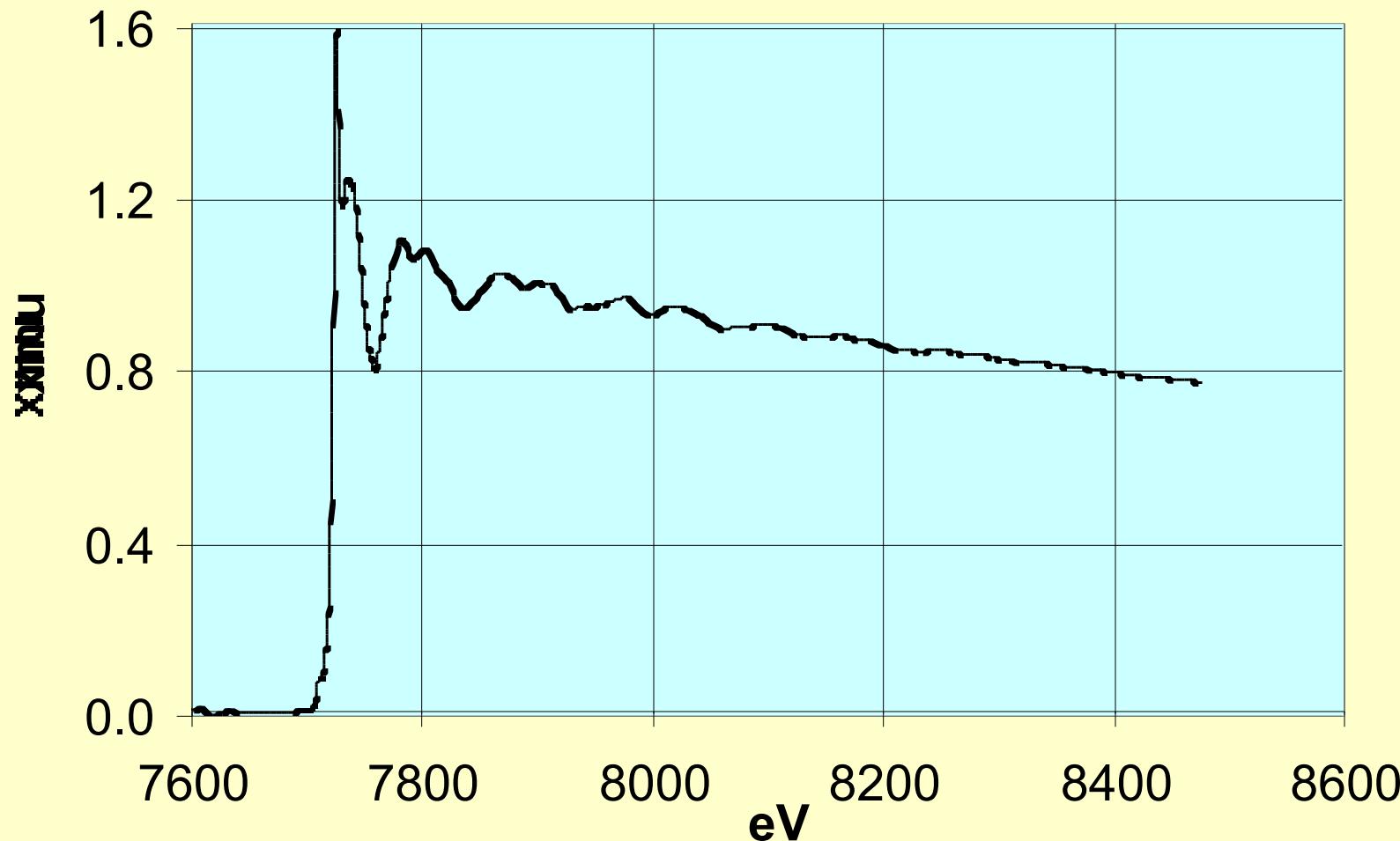
### Co K-edge of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$

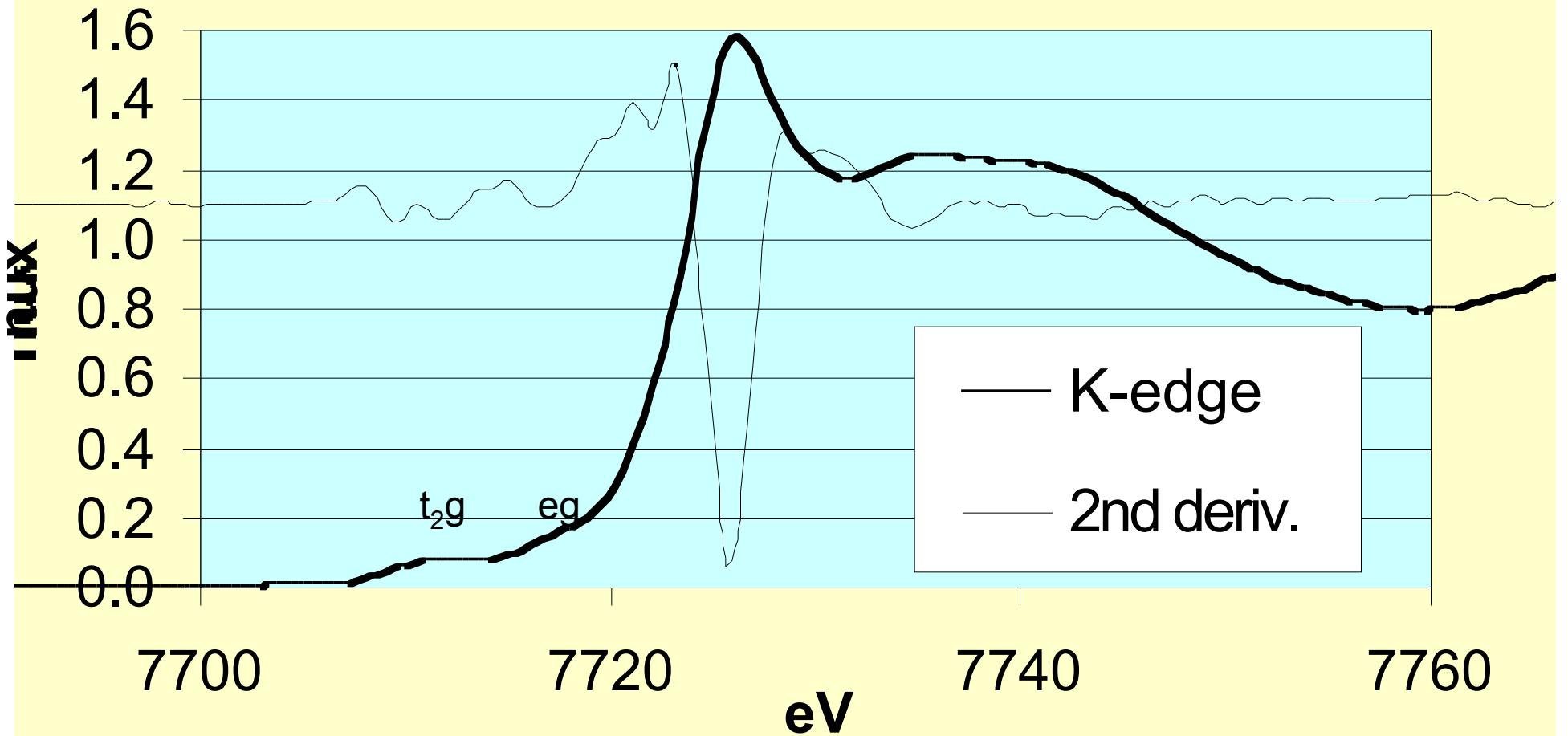


Co K pre-edge of  $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ 

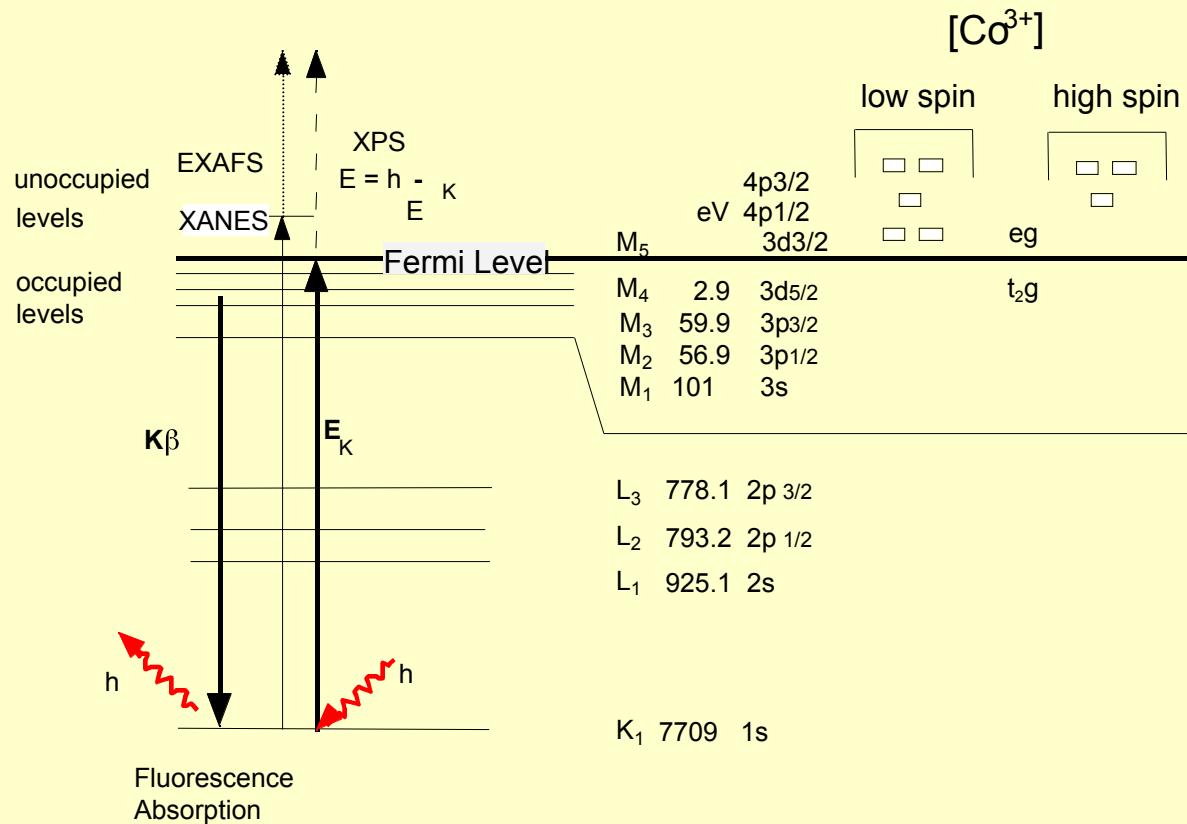
Fourier transform function of the EXAFS signal obtained from the  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  powder sampl

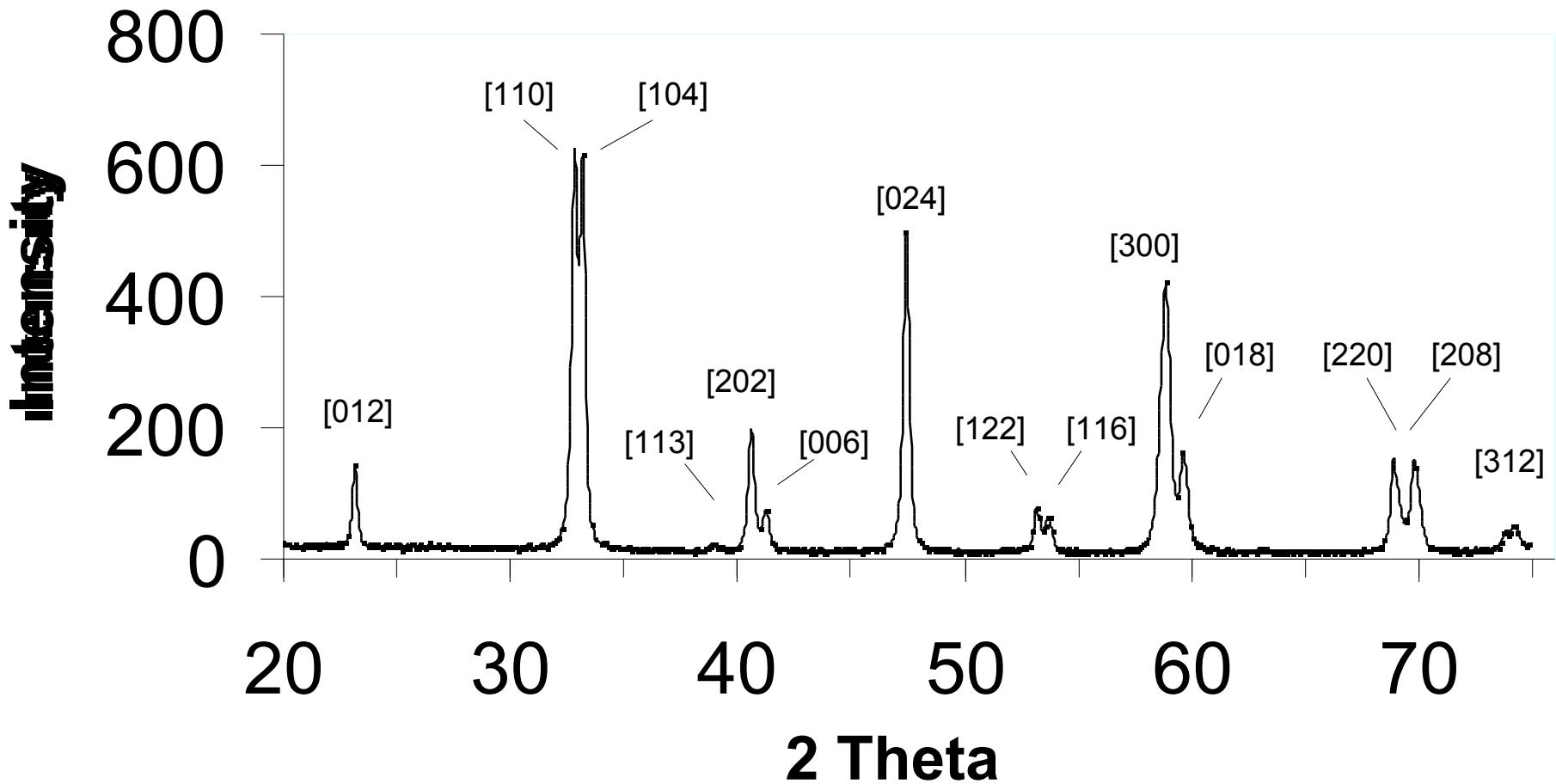
$\chi(r)$

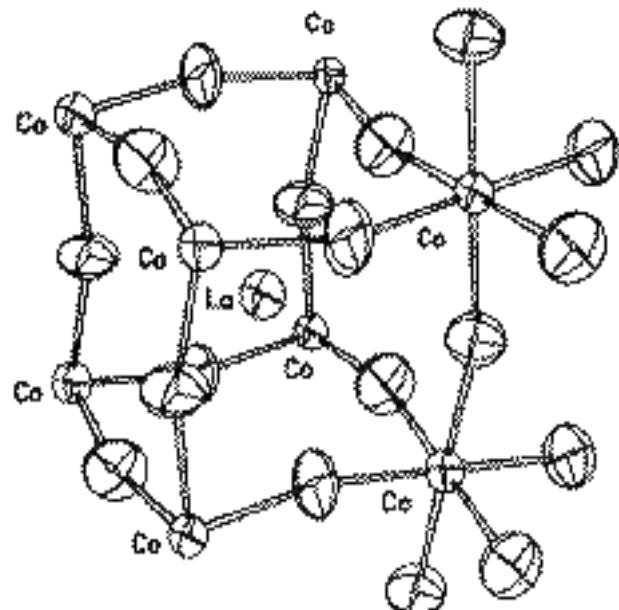
X-ray absorption LaCoO<sub>3</sub>

Co K-pre-edge LaCoO<sub>3</sub>

## Scheme of electron binding energies of Cobalt

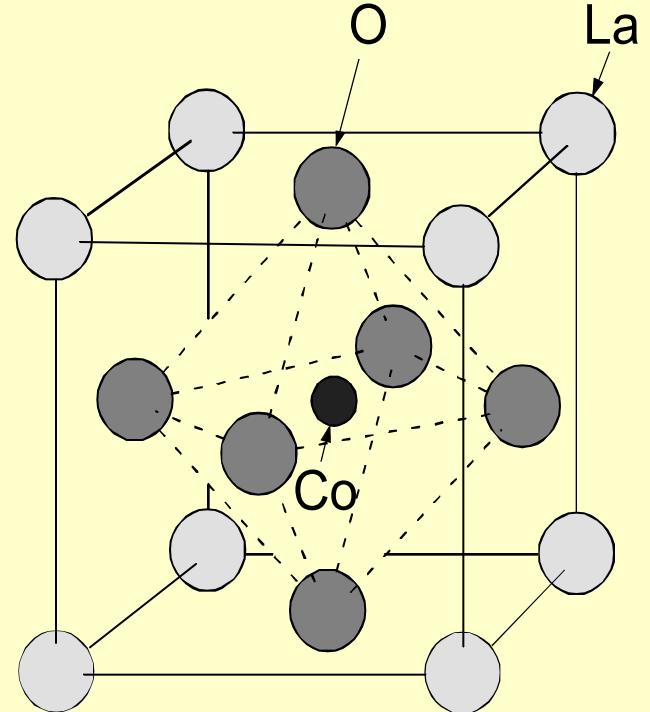


XRD LaCoO<sub>3</sub> Perovskite

Structure  $\text{LaCoO}_3$ 

Rhombohedral R-3C symmetry #167

G. Thornton et al. J. Solid State Chem. **61**, 301,  
(1986)



Cubic PM3M symmetry #221

**Table 1a:** Positions of the atoms with  $\text{LaCoO}_3$  based on R-3C (#167) space group symmetry with unit cell lengths  $a=b=c=5.3489 \text{ \AA}$  and angles  $\alpha = \beta = \gamma = 60.966^\circ$ . [M=Multiplicity; Wy=Wyckoff notation]  
(Thornton86).

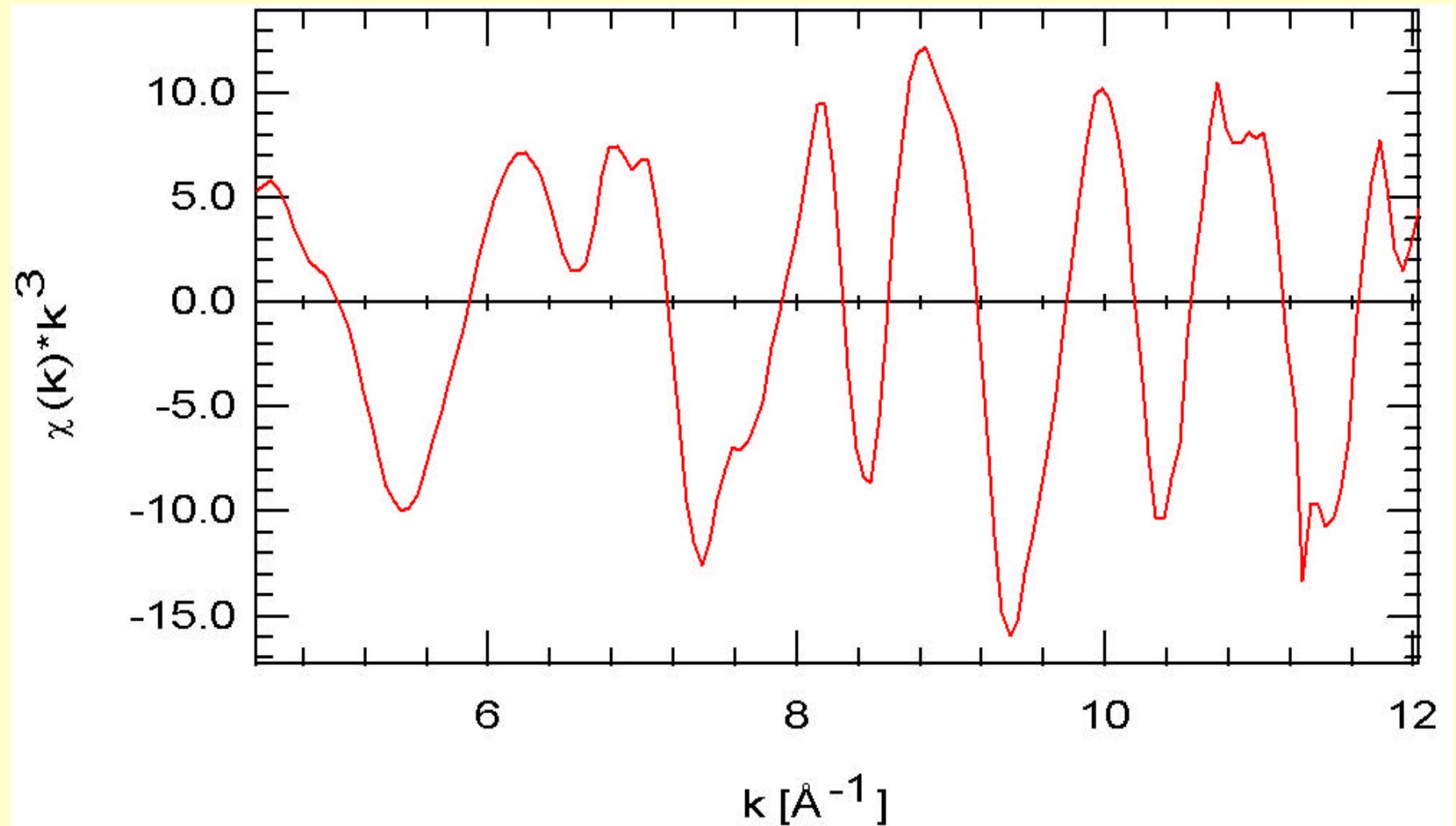
Atom	M (Wy)	X	Y	Z
La	2 (a)	0.25	0.25	0.25
Co	2 (b)	0.00	0.00	0.00
O	6 (e)	0.1982	0.3018	0.75

**Table 1b:** Positions of the atoms with  $\text{LaCoO}_3$  based on PM3M (#221) space group symmetry with unit cell lengths  $a=b=c=3.82 \text{ \AA}$  and angles  $\alpha = \beta = \gamma = 90^\circ$ . [M=Multiplicity; Wy=Wyckoff notation] (A.Wold+R.Ward J.Am.Chem.Soc, 76 (1954) p.1029-1030)

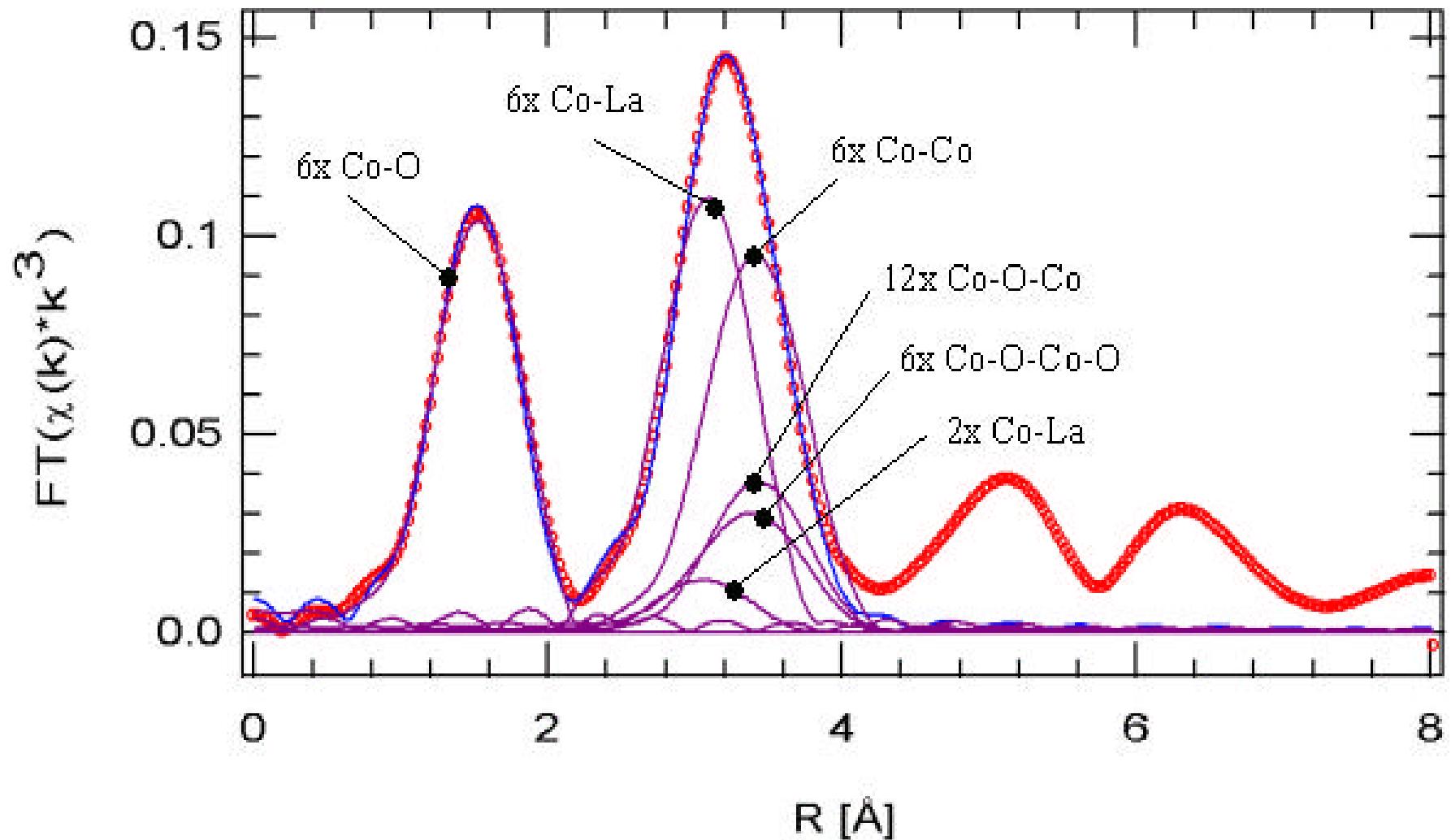
Atom	M (Wy)	X	Y	Z
La	1 (a)	0.0	0.0	0.0
Co	1 (b)	0.5	0.5	0.5
O	3 (c)	0.5	0.5	0.0

R-3C (#167)				PM3M (#221)			
Path	CN	R	CW ratio	Path	CN	R	CW ratio
Co-O	6	1.9318	100	Co-O	6	1.91	100
Co-La	2	3.2732	16.1	Co-O-O	24	3.2606	16.4
Co-O-O	12	3.2831	8.4	Co-La	8	3.3082	61.8
Co-O-O	12	3.3125	8.0	Co-Co	6	3.82	20.9
Co-La	6	3.3263	46.5	Co-O-O	6	3.82	16.2
Co-Co	6	3.8256	21.3	Co-O-Co	12	3.82	57
Co-O-Co	12	3.8447	47.2	Co-O-Co-O	6	3.82	12.8
Co-O-La	12	3.8545	5.5	Co-O-Co-O	6	3.82	5.5
Co-O-O	6	3.8637	16.1	Co-O-Co-O	6	3.82	39.2
Co-O-Co-O	6	3.8637	12.3	Co-O-Co-O	24	3.82	< 2.7
Co-O-Co-O	6	3.8637	5.5	Co-O-La	48	3.9597	16.6
Co-O-Co-O	6	3.8637	27.6				

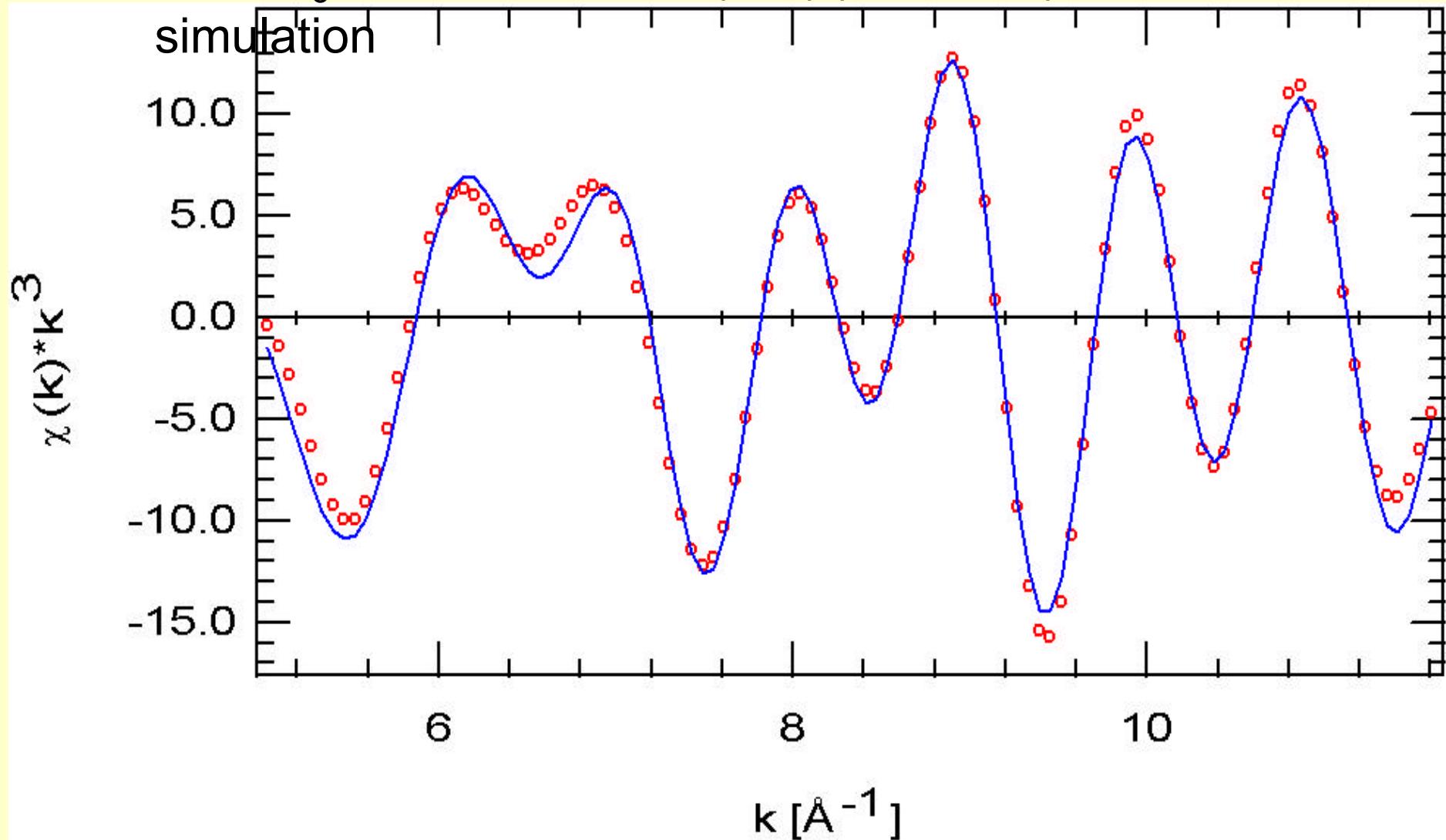
# Normalized, background-subtracted and $k^3$ -weighted LaCoO<sub>3</sub> XAFS Spectrum ( $k^3$ ( $k$ )-function)



## Radial structure function (RSF) obtained by Fourier transformation of $k^3$ ( $k$ ) with FEFF8 code simulation



Normalized, background-subtracted and  $k^3$ -weighted  
LaCoO<sub>3</sub> XAFS Spectrum ( $k^3$  ( $k$ )-function) with FEFF8 code



Structural parameters for  $\text{LaCoO}_3$  derived from the Co K-edge EXAFS analysis

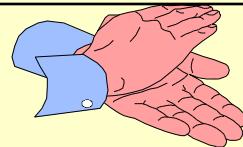
R-3C (#167)			$E_o = -0.16 \text{ eV}$ Residual=4.43%		$E_o = +0.47 \text{ eV}$ Residual=11.9%	
			<== R-space fit ==>		<== k-space fit ==>	
Sphere	Shell	CN *	R	$-^2$	R	$-^2$
1 <sup>st</sup>	Co-O	6	1.9176	4.79	1.9196	5.14
2 <sup>nd</sup>	Co-La	2	3.2732 *	12.8	3.2732 *	>> 10 **
2 <sup>nd</sup>	Co-La	6	3.3263 *	5.70	3.3263 *	6.17
2 <sup>nd</sup>	Co-Co	6	3.8256 *	10.4	3.8256 *	5.88
2 <sup>nd</sup>	Co-O-Co	12	3.8447 *	9.86	3.8447 *	7.23
2 <sup>nd</sup>	Co-O-Co-O	6	3.8637 *	14.9	3.8637 *	6.43

Structural parameters for  $\text{LaCoO}_3$  derived from Co EXAFS analysis:  
Phase shifts ( $\_E_o$ , eV), Residuals (%), Interatomic distances (R, Å),  
Coordination numbers (CN), and Debye-Waller factors ( $\_2$ ,  $\text{\AA}^2 \cdot 10^{-3}$ )

PM3M (#221)			$\_E_o = -0.98 \text{ eV}$ Residual=4.71%		$\_E_o = -1.63 \text{ eV}$ Residual=16.0%	
			<== R-space fit ==>		<== k-space fit ==>	
Sphere	Shell	CN <sup>*</sup>	R	$\_2$	R	$\_2$
1 <sup>st</sup>	Co-O	6	1.9150	4.96	1.9105	5.38
2 <sup>nd</sup>	Co-La	8	3.3204	6.86	3.3205	7.32
2 <sup>nd</sup>	Co-O-Co	12	3.82 *	20.0	3.82 *	19.5
2 <sup>nd</sup>	Co-O-La	48	3.9597 *	0	3.9597 *	0

Scattering paths, coordination numbers (CN), interatomic distances (R, Å) and estimated coordination weight ratios (CW ratio, %) for the first two coordination shells. The data were generated with the FEFF 8 code and the structural data for space group R-3C, respectively,

PM3M R-3C (#167)				PM3M (#221)			
Path	CN	R	CW ratio	Path	CN	R	CW ratio
Co-O	6	1.9318	100	Co-O	6	1.91	100
Co-La	2	3.2732	16.1	Co-O-O	24	3.260	16.4
Co-O-O	12	3.2831	8.4	Co-La	8	3.308	61.8
Co-O-O	12	3.3125	8.0	Co-Co	6	3.82	20.9
Co-La	6	3.3263	46.5	Co-O-O	6	3.82	16.2
Co-Co	6	3.8256	21.3	Co-O-Co	12	3.82	57
Co-O-Co	12	3.8447	47.2	Co-O-Co-	6	3.82	12.8
Co-O-La	12	3.8545	5.5	O Co-O-Co-	6	3.82	5.5
Co-O-O	6	3.8637	16.1	O Co-O-Co-	6	3.959	39.2
Co-O-Co-	6	3.8637	12.3	O Co-O-Co-	24	3.82	< 2.7
O Co-O-Co-	6	3.8637	5.5	O Co-O-La	48	3.959	16.6
O Co-O-Co-	6	3.8637	27.6	O	7		



# Acknowledgements



Dr. Rudolf Struis   Stefan Müller   Franziska Holzer   Gertraud Masanz  
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